

A microstructural analysis of orientation variation in epitaxial , AlN on Si, its probable origin, and effect on subsequent GaN growth

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Abstract

A structural examination of aluminum nitride growth on [111] silicon was carried out using transmission electron microscopy. Electron diffraction indicates that the basal planes of the wurtzitic overlayer mimic the orientation of the close-packed planes of the substrate. However, considerable, random rotation in the basal plane and random out of plane, tilts of about $\pm 3-4^\circ$ are evident. The orientation variations were traced to the Si interface, where crystalites and an amorphous-like background were present. A strong relationship between these phenomena and substrates containing Si is established by comparing the present growth results with those reported elsewhere. Crystalline quality of the overgrown GaN on the AlN layer is described, with suggestions for the relation between surface pyramids or peaks and the mis-oriented buffer layer.

Introduction

Gallium nitride and aluminum nitride epitaxial films show great promise for use in optoelectronic and high power devices due to their large, direct band-gaps corresponding to blue anti ultraviolet wavelength regime. Before such devices can be realized, reliable growth methods are needed that produce epitaxial layers of device quality. Thus far, heteroepitaxy is the only practical means, anti much progress has been achieved with sapphire substrates [1]. optimally, substrates are needed that are defect-free, cleave and etch well, are inexpensive, anti are available with large surface areas. Silicon is thus an attractive candidate.

The direct deposition of GaN on silicon results in unacceptably high surface roughness and poor crystal quality. Aluminum nitride buffer layers have been employed to improve the GaN quality [2,3]. Epitaxial AlN is readily grown to have a flat surface on silicon, and has been reported to be able to grow as a single crystal [2,3]. The quality of GaN on AlN is known to be dependent upon the buffer layer growth conditions [3,4], but uncertainties remain about the nature of the AlN quality and how it influences subsequent GaN overgrowth. This article examines these issues with a structural examination of AlN and GaN/AlN on silicon anti compares the findings to those reported in the literature.

Experimental

Single crystal AlN was first deposited over the Si(111) substrates using reactive MBF₃. The samples were analyzed using RHEED to confirm the single crystal nature of the sample surface. Subsequently, GaN was grown over the AlN coated Si(111) samples using conventional low pressure MOCVD. A growth temperature of 800°C anti a pressure of 76 Torr were employed and TEGa and N₂ were used as precursors. (cross-sectional samples for TEM were prepared for viewing by gluing the grown layers face-to-face with M-bond epoxyTM[5]. The orientation of the material was such that a slice of each sandwich had a surface normal of [1120] on one side of the epoxy and [1100] on the other. Discs were ultrasonically cut from each slice with a diameter of 2.3 mm and subsequently glued into brass rings of 2.3 mm I.D. anti 3.0 mm O.D.) to enhance

mechanical stability. Discs were then thinned to 50 μm and dimpled on one side to about 10 μm before ion milling both sides to electron transparency. Plan view samples were prepared by first coring the material in a direction parallel to the substrate surface normal and gluing into rings as before. All thinning was performed as with the cross-sectioned samples, but taking place only on the silicon side. All TEM work was performed with a Topcon 002B using both high-resolution and high-tilt polepieces, depending on the need.

Results

AlN on Si- Figure 1 is a selected area electron diffraction pattern (SAEDP) obtained from a cross-sectional sample, illustrating the observed orientation relationship between substrate and AlN layer:

$$\begin{aligned} (111)\text{Si} // (0002)\text{AlN} \\ [\bar{1}10]\text{Si} // [11\bar{2}0]\text{AlN} \end{aligned}$$

This relationship is the same as that between hexagonal and cubic structures that differ only in the stacking sequence of the close-packed planes. Extensive tilting experiments were performed to examine the possibility of the $(0002)\text{AlN}$ assuming the orientation of one of the other $[11\bar{1}]\text{Si}$ variants inclined to the interface, as well as the existence of cubic AlN. The basal plane normals of the wurtzite AlN were indeed found to lie parallel to the surface normal of the silicon throughout, but with $\pm 3\text{--}4^\circ$ tilt variation, witnessed by the arcs (not spots) of the AlN diffraction pattern of Figure 1. No SAD evidence of cubic AlN presence was observed in the cross-sectional samples, although cubic spots are masked in some orientations.

Figure 2 is a bright-field image taken from the same region as Figure 1, demonstrating the overall appearance of the AlN layer, the outer surface of which is essentially flat. Orientation variations throughout the layer result in the Moiré patterns being observed in high-resolution images. Figure 3 shows that the observed tilts extend to within a monolayer of the interface, with at least $\pm 3\text{--}4^\circ$ tilt variation as witnessed in the diffraction patterns. Figure 3 also shows that the basal plane tilting is not continuously varied, but rather confined to discrete crystallites, randomly mis-aligned with respect to the Si template. A thin, anisotropic-like region at the Si interface is also seen in this and other images.

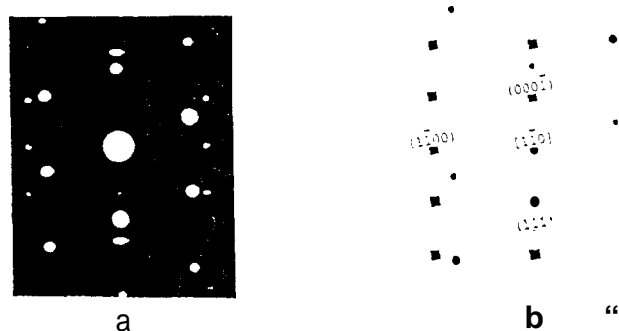


Figure 1: Experimental (a) and simulated (b) SAEDP of AlN on Si with the orientation relationship described in the text. Silicon reflections are shown as circles, AlN as squares.

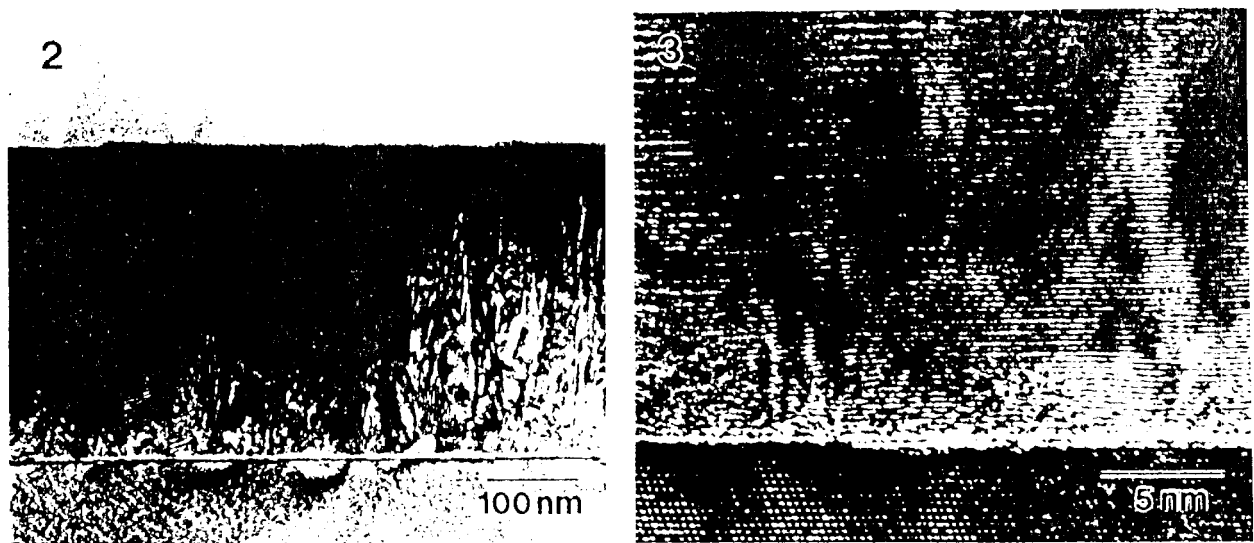


Figure 2: TEM cross-section bright-field image of AlN on Si, showing smooth outer surface, and representing the area from which Figure 1 was obtained. The AlN band is seen between Si (below) and TEM specimen preparation epoxy (above).

Figure 3: High-resolution image at the AlN/Si interface, showing tilted AlN crystallite (upper layer) corresponding to the arcs observed in Figure 1.

Plan-view samples yielded similar results. Figure 4a is a SADP of a plan-view sample at the $[11\bar{1}]$ pole of silicon, confirming the above orientation relationship. In addition to the tilt of the AlN basal planes described above, this SADP shows extensive rotation in plane. Figure 4c was taken near the region represented in Figure 4a, but in an area thin enough to allow only AlN reflections. Rotation in the basal plane is seen to be much more extensive than tilting out of plane and nearly results in continuous rings connecting the reflections of lowest index. Figure 5 is a plan-view bright field image of the AlN layer. Here, the extensive in-plane rotation suggests a polycrystalline microstructure.

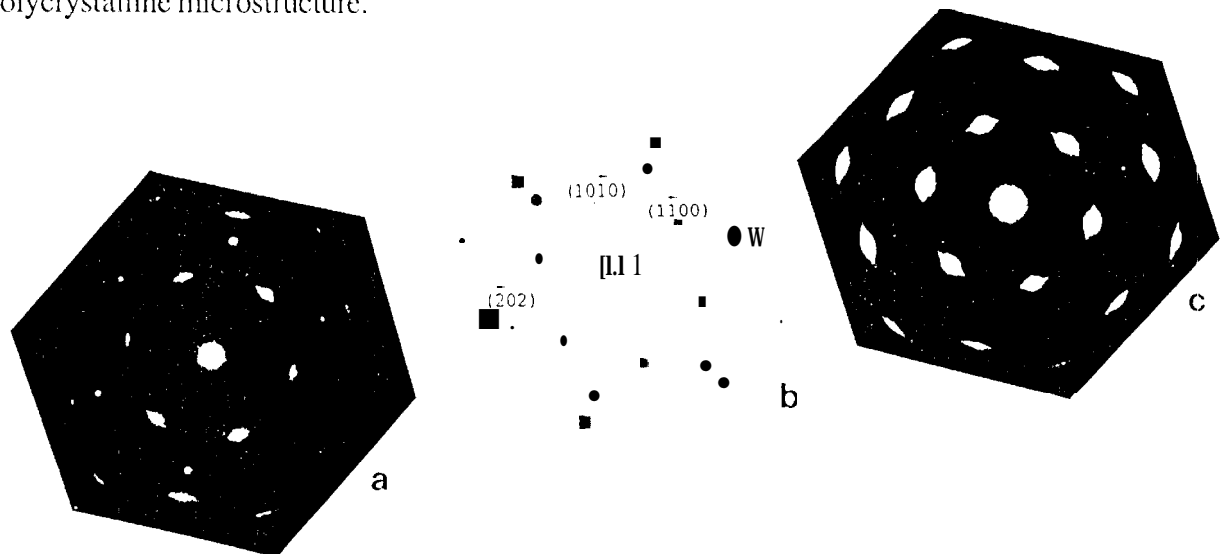


Figure 4: Experimental (a) and simulated (b) SADP of AlN on Si with electron beam direction parallel to substrate surface normal, confirming the relationship seen in cross-section, and showing extensive in-plane rotation. Silicon reflections are shown as circles, AlN as squares. Experimental (c) SADP taken nearby, showing only AlN material with much streaking.

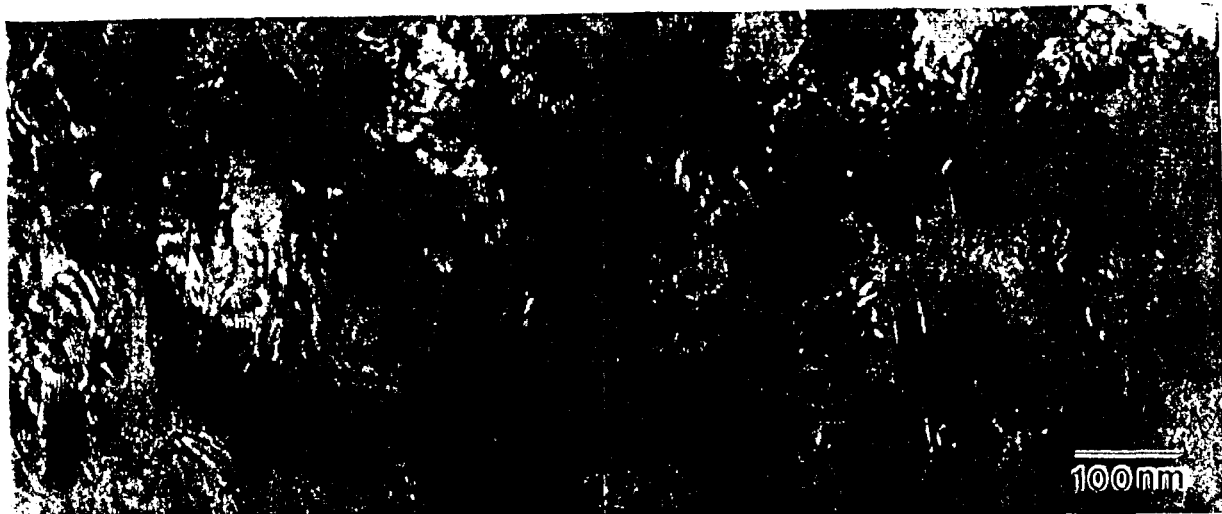


Figure 5: TEM plan-view image of AlN as in Figure 4. Features resembling grains are of similar scale as those seen in Figure 2.

That the angular range at the interface resembles that throughout the AlN suggests a correlation between the interracial AlN domains and bulk mis-alignment. Basal d-spacings vary negligibly, while their orientation varies considerably, further substantiating this suggestion that the mis-oriented AlN nuclei are seeds for subsequent mis-orientation in the layer. This correlation has not been previously established, nor have the origins of the interfacial effects themselves. However, articles by other authors indicate similar interfaces, and similar diffraction patterns. Mis-alignment of GaN crystallite at the silicon interface and an amorphous-like region are seen between extended substrate surface steps in a study examining the effects of Si surface cleanliness on GaN growth. The authors minimized surface contamination by cleaning the substrates using an RCA cleaning procedure followed by an HF dip [6]. Another study [7] shows a SAIDP at the AlN/Si interface with much the same tilt, and describes an amorphous layer for AlN or GaN on Si, but not on sapphire. The authors report that analytical electron microscopy (AEM) found no oxide at the Si substrate. Ponce, et al. [8], describe similar interracial AlN nuclei on SiC, whose mis-orientations become distributed throughout the AlN layer. It appears, then, that these orientation and amorphous-like domains are not the result of surface contamination or surface roughness, but rather of an inherent chemical or mechanical effect in the Al (or Ga)-N-Si system. The lattice mismatch between SiC and AlN is very small 0.11% the basal plane (about 1%) while that for a silicon substrate is significant (mismatch = 19%). Crystallite tilting occurs for both substrates suggesting that lattice mismatch is not the cause of the tilting. It should be noted that this effect is not observed on sapphire (mismatch $>13\%$). Furthermore, as these effects are associated with silicon-bearing substrates, interfacial Si-bonding appears to be a likely cause.

The formation of amorphous silicon nitride during the initial stages of AlN growth would result in preferential alignment of the nuclei with the Si template, but with random tilt and rotation excursions proportional to the amount of Si_3N_4 formed. One reason AlN is preferred over GaN as an initial layer is due to the increased stability of AlN with respect to Si_3N_4 formation. Bulk thermodynamic calculations show that AlN is more stable than Si_3N_4 in the Al-N-Si environment [9], as opposed to Ga-N-Si system, in which Si_3N_4 is reportedly more stable [?]. However, interfacial tilts, rotations, and the amorphous-like region are seen for both systems. It then stands to reason that either silicon nitride formation is occurring in both systems, or silicon nitride, is not responsible for the interfacial phenomena. In the latter case, silicon presence may still interfere with nucleation through chemical interactions at the interface such that the ideal AlN/Si orientation relationship is disrupted. Silicon has been reported to diffuse into GaN on Si at temperatures as low as 600°C [10]. Although diffusion is not expected to affect the orientation of already formed nuclei, such findings do indicate an affinity between Si and the AlN lattice. Interestingly, in the same study, similar interfaces are described, with Si concentrations 0.11% the order of several atomic percent at distances into the GaN similar to those of the disordered layer. One possible explanation

for what happens at the interface involves a combination of both views. In this scenario, the surface Si and N combine, the product of which then attempts to mimic the Si template, but is restricted by the Si-N bonding. Subsequently, Al(or Ga)N is grown upon this best-fit arrangement. Such a situation would help to explain how the closed-packed plane and direction information is transmitted across the tilted, rotated, and amorphous-like interracial region. Further investigation is needed to determine if the Si is indeed responsible for the rotated domains and, if so, whether it is from simple lattice distortion or a particular reaction with one of the epitaxial layer species.

GaN on AlN on Si-

With the texturing nature of the AlN layer established, growth of subsequent GaN is briefly described. Figure 6 shows a heavily faceted surface and polycrystalline microstructure belonging to the GaN. The peak surfaces are along $\{10\bar{1}1\}$ planes, corresponding to angles of 62° with respect to the basal planes. Such peaks may be related to Ga surface migration and evaporation from $\{10\bar{1}1\}$ planes [11]. In this case, when two-dimensional growth is interrupted, $\{10\bar{1}1\}$ surfaces may become established. Gallium may then easily evaporate and thus provide a slower-growing surface than that of the basal-plane. The basal plane, bounded by $\{10\bar{1}1\}$ surfaces grows until the surfaces converge, leaving a hexagonal pyramid. Initiation of a three-dimensional surface may arise from areas of GaN of opposite polarity [12], growing at a different rate; or from the intersection of grains or regions with slight orientation differences; or from dislocations at the surface. It is expected that the large tilts and rotations of the AlN basal planes of the buffer layer are largely responsible for the rough GaN surface. Efforts to mitigate this effect are underway.



Figure 6: Cross-section TEM bright-field image of GaN on AlN on Si, showing a heavily faceted outer surface, corresponding to $\{10\bar{1}1\}$ planes.

Conclusions

In this work, the exact nature of the AlN buffer layer on silicon orientation variation has been established. It has been shown that, throughout the buffer layer, tilts of basal plane normals randomly deviate from the Si (111) surface normal by within approximately $\pm 3-4^\circ$, while rotations in plane were shown to rotate randomly with the approximate range of $\pm 10^\circ$. These deviations were shown to extend to the substrate surface, where a region of crystallite in a background of an amorphous-like appearance was present. It has been suggested that the interracial phenomena are the responsibility of the chemical bonding from the Si-bearing substrate, and may encourage the formation of $\{10\bar{1}1\}$ peaks on subsequently grown GaN.

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